Bound States of ^{3}He at the Helium-Cesium Interface

D. Ross, P. Taborek, and J. E. Rutledge
Department of Physics, University of California, Irvine, California 92717

(Received 20 January 1995; revised manuscript received 1 March 1995)

We have measured the wetting phase diagram of ^{3}He-^{4}He mixtures on cesium between 0.6 and 2.1 K, the pure ^{4}He wetting temperature. The surface tensions which determine the wetting behavior are strongly dependent on the surface excess of ^{3}He. The wetting phase diagram shows that there are bound states of ^{3}He at the Cs-He interface, analogous to the Andreev states at the liquid-vapor interface. The binding energy of these states is approximately 2 K.

PACS numbers: 67.70.+n, 68.45.Gd

For most of this century the binding between two helium atoms was believed to be the weakest of atomic interactions. Consequently, superfluid helium was expected to wet all surfaces. In 1991 Cheng *et al.* [1] predicted that because the interaction between helium and an alkali metal could be even weaker than the helium-helium interaction, ^{4}He would not wet the heavier alkali metals at zero temperature. This prediction sparked a number of studies [2] of weak binding substrate systems. In particular, the ^{4}He-Cs system demonstrates the complete thermodynamics of a first-order wetting transition more clearly than any other system [3].

Wetting is governed by surface tensions. At the wetting transition the contact angle vanishes, so

$$\sigma_{lv} = \sigma_{sv} - \sigma_{sl}\,, \tag{1}$$

where the $\sigma_{\alpha\beta}$ are surface tensions. The indices l, v, and s stand for liquid, vapor, and substrate, respectively. The interaction between the adsorbate and substrate contributes to the surface tension difference on the right-hand side of Eq. (1). The wetting phenomena displayed by the He-Cs system are the result of the small size of this difference. A valuable feature of the He-Cs system is that the surface tensions can be experimentally manipulated. The substrate interaction strength can be tuned by varying the thickness of a cesium overlayer on a strong-binding substrate [4]. Using this technique, the right-hand side of Eq. (1) can be varied from the weak-binding to the strong-binding limit [5]. σ_{lv}, the left-hand side of Eq. (1), can also be experimentally controlled by the addition of ^{3}He to the ^{4}He film [6]. Pettersen and Saam [7] have shown that this results in reentrant wetting, i.e., wetting at low and high temperatures and nonwetting at intermediate temperatures. This feature has been experimentally confirmed [8].

The addition of ^{3}He can also affect the right-hand side of Eq. (1). Because the minimum in the He-cesium surface potential is so far from the cesium surface and so weak, the He-Cs interface has been thought to resemble the free surface of the liquid more closely than the highly compressed liquid at a strong-bonding surface. This viewpoint suggests the possibility of bound, two-dimensional ^{3}He quasiparticle states at the He-Cs interface in analogy to the Andreev states at the free surface [6]. Density functional calculations, in fact, predict strongly bound 2D ^{3}He states at weak-binding surfaces with binding energies comparable to the Andreev state binding energy [9,10]. If these bound states exist, it may be possible to create films with a ^{3}He-^{4}He-^{3}He sandwich structure, which would be a rich experimental system. Such deeply bound surface states should have a profound effect on wetting properties of ^{3}He-^{4}He mixtures. Pettersen and Saam [7] have shown that a measurement of the ^{3}He concentration needed to induce wetting would both test the existence of bound ^{3}He states at the He-Cs interface and measure their binding energy if they indeed exist.

We present here the first complete measurements of the wetting phase diagram of dilute solutions of ^{3}He in ^{4}He on cesium, from 0.6 to 2.1 K. Our data confirm the existence of bound ^{3}He states at the He-Cs interface. The binding energy is near 2 K.

Our experimental techniques are similar to those we used to study pure ^{4}He and have been described before [3,11]. The cesium surfaces studied in this experiment were made by evaporating pure cesium metal onto the mass sensitive regions of a quartz crystal microbalance at a rate of ~0.01 monolayer/s. The microbalance and the vacuum can in which it was contained were maintained at a temperature less than 6 K throughout the evaporation process to eliminate contamination of the highly reactive cesium surface. After the cesium surface was prepared, the frequency shift of the quartz microbalance measured the amount of helium adsorbed on it with a mass resolution of 0.05 layer. A resistive heater on the microbalance allowed it to be heated above the ambient temperature to remove the helium film. A second microbalance with gold electrodes was also contained in the vacuum can. The data shown here were taken on two different Cs substrates with identical ^{4}He wetting temperatures of 2.09 K.

Our experiment is a measurement of the wetting temperature, T_w, as a function of the ^{3}He concentration in the bulk liquid, X_3. All of the measurements were made

0031-9007/95/74(22)/4483(4)$06.00

at liquid-vapor coexistence with bulk liquid ^{3}He-^{4}He mixture in the bottom of the vacuum can. The frequency shift of the oscillator was used to determine whether the cesium surface was wet or nonwet. Hysteresis in the frequency shift was used to determine T_w. As has been shown previously [3], the amount of helium adsorbed on the cesium is hysteretic. When the wet state is thermodynamically stable, an arbitrarily thick film of liquid is always adsorbed. If the system starts in the wet state and is cooled into a region where the nonwet state is stable, the film does not spontaneously become nonwet. Nonwetting requires the nucleation of a patch of thin film which is energetically so costly that the metastable thick film persists indefinitely. If the nonwet state is stable but a metastable wet film covers the substrate, a momentary heat pulse applied to the substrate creates a thin patch and switches the film into the nonwet state. In contrast, if the temperature of a stable nonwet film is changed to a region where the wet state is stable, the film spontaneously thickens. Because the cesium film forms an island on a quartz surface, a thick film is always present at the edges of the cesium. This film spontaneously nucleates the wet state. Hysteresis loops can be generated by changing the temperature of the experiment and applying appropriate heat pulses to the substrate. The hysteresis loops close at T_w.

Figure 1 shows an example of a hysteresis loop that closes at two temperatures, demonstrating reentrant wetting. Starting at 1.1 K the heater was pulsed to establish the nonwet equilibrium thickness. Then the experiment was cooled to 0.8 and returned to 1.1 K. At each point, the temperature was held constant and the resonant frequency of the microbalance and the pressure were monitored until they stopped drifting. As the experiment was cooled to 0.8 K, the frequency shift shows that the film thickens, wetting the substrate. As the wet film is warmed to 1.1 K, the film thickness diverges from its path along the cooling curve at 0.88 K. This establishes 0.88 K as a wetting temperature and shows that the equilibrium state is nonwet above 0.88 K. The upper wetting temperature for this mixture, 1.73 K, was determined similarly. The pressure and the adsorbed mass on the gold oscillator remained single valued throughout this cycle, which demonstrates that concentration equilibrium was maintained.

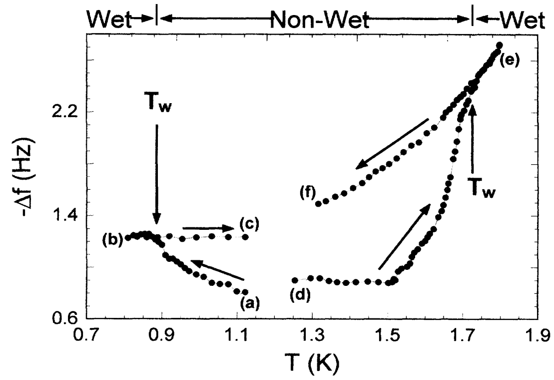

FIG. 1. Frequency shift vs temperature for wetting temperature measurement. Starting at point *a* with a nonwet surface, the experiment is cooled below the wetting temperature to point *b*. Because the thick film state is metastable, the surface remains wet as the temperature is raised back above the transition temperature to point *c*. The wetting temperature is identified as the point where the hysteresis loop closes. A heat pulse applied to the substrate moves the film from point *f* to point *d*. The *d*-*e*-*f* loop locates the upper wetting temperature. The slope of $-\Delta f$ vs T is due to the temperature dependence of the normal fraction.

The measurement of X_3 was done in two ways. At temperatures above 1.3 K, the pressure and temperature were monitored and the boiling curves of Sydoriak and Roberts [12] were used to determine X_3. At lower temperatures, where the boiling pressure was too low to be measured reliably, sufficient helium of known total concentration was admitted to the cell so that it was approximately 10% filled with liquid. X_3 was then calculated from the volume of the cell, the amount of helium in it, and the total concentration. These two measurement techniques were checked against each other between 1.2 and 2 K and found to agree within 0.2%.

The hysteresis loops and the concentration measurements are combined to give the phase diagram in Fig. 2. Uncertainties in establishing the closing point of the hysteresis loops result in roughly 10 mK uncertainties in the temperature at each measurement. These errors and thermometry uncertainties, which are largest near 1.3 K in our case, translate into concentration errors because of the temperature dependence of the boiling curves. The error

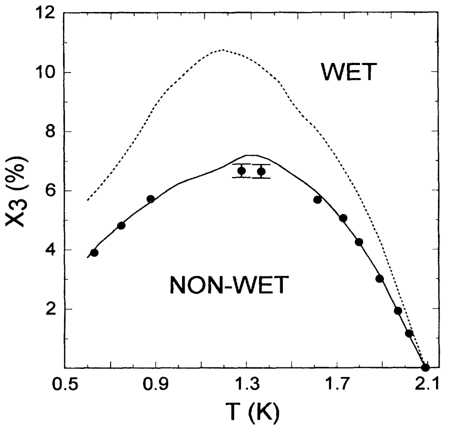

FIG. 2. The X_3 vs T_w wetting phase diagram for ^{3}He-^{4}He mixtures on Cs. The dashed curve is calculated from Eq. (1) assuming no bound state at the He-Cs interface. The solid curve is a best fit and includes a ^{3}He state at the He-Cs interface with a binding energy of 1.95 K. In the region below the curve the cesium surface is nonwet. Above the curve it is wet.

bars near 1.3 K are shown in Fig. 2. The errors in the other data points are the size of the plotting symbols.

Equation (1) defines a phase boundary which can be compared to the data of Fig. 2. Since the liquid-vapor surface tension $\sigma_{lv}(X_3, T)$ has been independently measured [13,14], and the substrate-vapor surface tension σ_{sv} is expected to depend only weakly on T and X_3, the predicted shape of the phase diagram is determined by the behavior of the substrate-liquid surface tension, $\sigma_{sl}(X_3, T)$. Equation (1) determines this quantity at each data point. Unfortunately, a straightforward analysis of this data paralleling Andreev's analysis of the free surface is not possible. Andreev's analysis is based on a set of measurements of $\sigma_{lv}(X_3, T)$, where X_3 was varied from 0 to 0.2 independently of T. This allows the ^{3}He contribution to σ_{sl} to be separated from the temperature dependence of the pure ^{4}He background. Because our experiment determines σ_{sl} at only a single X_3 at each temperature, we must extract the ^{3}He contribution to σ_{sl} by considering the physical processes that determine the surface tension.

In general, there are contributions to the surface tension from two-dimensional quasiparticles at the surface and from the three-dimensional quasiparticles in the bulk of the material. The bulk states contribute because the boundary conditions at the surface make changes in the bulk quasiparticle density of states that result in contributions to the thermodynamic quantities that are proportional to the area [15]. The bulk excitations, phonons, rotons, and in the case of mixtures, ^{3}He quasiparticles, are reflected back into the liquid at either the free surface or the He-Cs interface. As a result, we expect the bulk contributions to the surface tensions at both interfaces to be quantitatively comparable. On the other hand, we expect the contributions from the two-dimensional excitations to be sensitive to the details at the surface and to differ. The two-dimensional excitations on the free surface of a helium mixture are ripplons and ^{3}He quasiparticles in the Andreev states. We expect linearly dispersed quantized Stoneley waves to replace ripplons at the He-Cs interface. We must also expect the effective mass and binding energy of bound states at the He-Cs interface to differ from their values at the free surface, including the possibility that there are no ^{3}He bound states at the He-Cs interface.

These considerations suggest that $\sigma_{lv}(X_3, T)$ is a reasonable zeroth-order estimate of $\sigma_{sl}(X_3, T)$. The estimate is refined by accounting for differences in the surface excitations. First we subtract the ripplon part of the surface tension [13] and add a contribution appropriate for Stoneley waves [16]. For finite X_3 we subtract the contribution from bound Andreev states [15] and add a term of identical form, but characterized by a new binding energy and effective mass. The effective mass and binding energy are determined by fitting the estimate of $\sigma_{sl}(X_3, T)$ to the data in Fig. 2 by means of Eq. (1). Our procedure differs from that of Pettersen and Saam, who assume that σ_{sl} is independent of temperature and equal to the zero temperature value of σ_{lv}, which has been the standard assumption in the theory [7].

We can show that our procedure for estimating σ_{sl} is reasonable by comparing it to values of $\sigma_{sl}(0, T)$ extracted from an earlier experiment. We have measured the wetting temperature of pure ^{4}He on a gold substrate covered with cesium films of varying thicknesses [17]. $\sigma_{sl}(0, T)$ can be extracted from those measurements [18] and compared with the estimate just described. First, rewrite Eq. (1) as

$$\Delta + \delta\sigma_{sl}(T_w) + \delta\sigma_{lv}(T_w) - \delta\sigma_{sv}(T_w) = 0, \quad (2)$$

where

$$\Delta \equiv \sigma_{sl}(0) + \sigma_{lv}(0) - \sigma_{sv}(0) \approx 2\sigma_{lv}(0) + \int_{z_{\min}}^{\infty} \rho(0)V(z)\,dz, \quad (3)$$

$\delta\sigma_{ij}(T_w) \equiv \sigma_{ij}(T_w) - \sigma_{ij}(0)$, and $\rho(0)$ is the number density of pure ^{4}He. $V(z)$ is the adsorption potential appropriate to a layered substrate [19] and $z_{\min}$ is the position of the minimum in $V(z)$. The approximate equality in Eq. (3) is verified by the full density functional treatment of the problem [1]. Since $\delta\sigma_{sv}(T)$ is negligible and $\delta\sigma_{lv}(T)$ is a measured quantity [13], Eqs. (2) and (3) can be solved for $\delta\sigma_{sl}(T)$. The results of this procedure are shown in Fig. 3, along with the solid line which results from estimating $\delta\sigma_{sl}(T)$ as described above. Our estimate is a reasonably accurate representation of the data.

In constructing $V(z)$ we have used standard values of well depths and van der Waals coefficients for ^{4}He on Au and Cs [20], except for the ^{4}He on Cs well depth. Here we have used a value of 7.4 K. This value is within the range spanned by other estimates of the

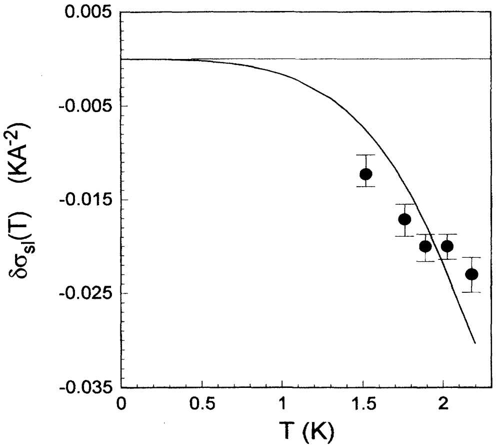

FIG. 3. The temperature dependence of $\delta\sigma_{sl}$. The solid curve is derived from $\sigma_{lv}(T)$ corrected for differences in the surface excitations, as described in the text. The line $\delta\sigma_{sl} = 0$ is the Pettersen and Saam assumption. The data points are derived from the data in Ref. [17].

well depth [21]. The slope of $\delta\sigma_{sl}(T)$ vs T is nearly independent of this choice for well depths within a few K of this value. Hence, our data are inconsistent with a temperature independent σ_{sl}. $\delta\sigma_{sl}(T)$ must approach 0 with vanishing slope as T approaches 0. Our choice of the well depth is roughly consistent with that requirement.

Applying our estimation procedure for σ_{sl} to the mixture data, including corrections for differences in the binding energy and effective masses at the two surfaces, generates a family of phase diagrams which can be compared to the data of Fig. 2. The dashed curve in Fig. 2 results from assuming that there is no contribution to σ_{sl} from bound ^{3}He states at the He-Cs interface. This curve grossly overestimates the nonwet portion of the phase diagram and qualitatively shows that a positive surface excess of ^{3}He at the cesium interface is required to reconcile the model and the data. The solid curve is a best fit to the data, which yields a value of 1.95 K for the binding energy and a value of $0.73m_3$ for the effective mass of ^{3}He quasiparticle forming a two-dimensional gas at the He-Cs interface. Statistical errors in these quantities are roughly ± 0.2 K and $\pm 0.2m_3$, respectively. Systematic errors are not included in these error estimates.

The results presented here are the first experimental consequences of the new bound state at the He-Cs interface predicted by Pavloff and Treiner [9,10]. They confirm the picture that a weak-binding substrate forms an interface with liquid helium which is more like the liquid-vapor interface than the highly compressed interface near a typical strong binding surface.

We thank M. W. Cole, L. Nosanow, and A. Maradudin for useful discussion. This work was supported by NSF Grant DMR-9223775.

---

[1] E. Cheng, M. W. Cole, W. F. Saam, and J. Treiner, Phys. Rev. Lett. **67**, 1007 (1991).

[2] E. Cheng, M. W. Cole, J. Dupont-Roc, W. F. Saam, and J. Treiner, Rev. Mod. Phys. **65**, 557 (1993), and references therein.

[3] J. E. Rutledge and P. Taborek, Phys. Rev. Lett. **69**, 937 (1992).

[4] E. Cheng, M. W. Cole, W. F. Saam, and J. Treiner, J. Low Temp. Phys. **89**, 739 (1992).

[5] P. Taborek and J. E. Rutledge, Phys. Rev. Lett. **71**, 263 (1993).

[6] A. F. Andreev, Zh. Eksp. Teor. Fiz. **56**, 1089 (1969) [Sov. Phys. JETP **29**, 585 (1969)].

[7] M. S. Pettersen and W. F. Saam, J. Low Temp. Phys. **90**, 159 (1993).

[8] K. S. Ketola and R. B. Hallock, Phys. Rev. Lett. **71**, 3295 (1993).

[9] J. Treiner, J. Low Temp. Phys. **92**, 1 (1993).

[10] N. Pavloff and J. Treiner, J. Low Temp. Phys. **83**, 331 (1991).

[11] P. Taborek and J. E. Rutledge, Phys. Rev. Lett. **68**, 2184 (1992).

[12] S. G. Sydoriak and T. R. Roberts, Phys. Rev. **118**, 901 (1960).

[13] M. Iino, M. Suzuki, and A. J. Ikushima, J. Low Temp. Phys. **61**, 155 (1985).

[14] K. N. Zinov'eva and S. T. Boldarev, Sov. Phys. JETP **29**, 585 (1969).

[15] D. O. Edwards and W. F. Saam, in *Progress in Low Temperature Physics,* edited by D. F. Brewer (North-Holland, Amsterdam, 1978), Vol. VIIa, pp. 282–369.

[16] L. Pricaupenko and J. Treiner, J. Low Temp. Phys. **96**, 19 (1994).

[17] P. Taborek and J. E. Rutledge, Phys. Rev. Lett. **71**, 263 (1993).

[18] We are grateful to M. W. Cole for suggesting this analysis.

[19] E. Cheng, W. M. Cole, W. F. Saam, and J. Treiner, J. Low Temp. Phys. **89**, 657 (1992).

[20] G. Vidali, G. Ihm, H.-Y. Kim, and M. W. Cole, Surf. Sci. Rep. **12**, 133 (1991).

[21] W. F. Saam, J. Treiner, E. Cheng, and M. W. Cole, J. Low Temp. Phys. **89**, 637 (1992).